THE IMPACTS OF RESIDENTIAL AREA AND CAGE CULTURE ON WATER AND SEDIMENT QUALITIES OF SEMARIANG BATU RIVER

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List of Abbreviations

SOD – Sediment oxygen demand

PSA- Particle size analysis

TKN- Total Kjeldahl Nitrogen

TP- Total Phosphorus

TOC- Total Organic Carbon

Cu- Copper

Zn- Zinc

Cd- Cadmium

Fe- Iron

Pb- Lead

Cr- Chromium

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The impacts of residential area and cage culture on water and sediment qualities of Semariang Batu River, Malaysia.

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Abstract

The residential area and village along the Semariang Batu River may impact the quality of the water and sediment. The objectives of this study were to determine water quality and sediment qualities of Semariang Batu River at different locations along the river and the characteristics of sediment at seven stations. The DO values ranged from 3.69 mg/l to 5.90 g/ml. SOD $_{20}$ ranged from 1.24 g O_2/m^2/day at station located near the residential area and village to 5.14 g O_2/m^2/day with the station near small construction work showing the highest SOD_{20} values. The TP values ranged from 103.0 mg/kg to 599.2 mg/kg in DW while TKN values of sediment ranged from 344.7 mg/kg to 570.6 mg/kg DW. The ranges concentration of heavy metals values (mg/kg) where Ni; 6.01-25.69, Pb; 3.88-14.76, Zn; 48.92-124.53, Cr; 18.23-39.83, Cu; 1.98-33.84 and Fe; 12831.6 - 32593.7 in dry weight. Cu, Zn and Pb recorded the highest concentration near the urban residential area and village. The highest TP and TKN were affected by discharges from urban housing area, village and cage culture activities.

Key words: Semariang Batu River, sediment oxygen demand, residential area, heavy metals, nutrients

Abstrak

Kawasan perumahan dan kampung di sepanjang Sg. Semariang Batu boleh menyumbang implikasi kepada kualiti sedimen. Objektif kajian ini adalah untuk menentukan kualiti air dan sedimen dari Sg. Semariang Batu pada lokasi yang berbeza di sepanjang sungai dan ciri-ciri sedimen di tujuh stesen. Julat nilai DO adalah dari nilai 3.69mg/l sehingga 5.90 mg/l. Julat nilai SOD $_{20}$ *adalah dari 1.24 g*O_2/m^2*/hari di stesen terletak hampir kawasan perumahan dan kampung sehingga 5.14 g*O_2/m^2*/hari dengan aktiviti pembinaan kecil yang menunujukkan nilai* SOD_{20} *yang tertinggi. Jumlah keseluruhan fosforus (TP) memberi nilai diantara 103.0 mg/kg to 599.2 mg/kg dalam jisim kering , sementara jumlah keseluruhan nitrogen (TKN) di dalam sedimen diantara 344.7 mg/kg to 570.6 mg/kg dalam jisim kering. Julat nilai kepekatan logam berat (mg/kg) dimana Ni; 6.01-25.69, Pb; 3.88-14.76, Zn; 48.92-124.53, Cr; 18.23-39.83, Cu; 1.98-33.84 and Fe; 12831.6 - 32593.7 dalam jisim kering. Kepekatan tertinggi Cu, Zn dan Pb direkodkan berdekatan dengan kawasan perumahan bandar dan kampung. Nilai fosforus dan nitrogen yang tinggi adalah kesan daripada sisa kumbahan dari kawasan perumahan bandar, kampung dan pemternakan dalam sangkar.*

Kata kunci: Sg.Semariang Batu, keperluan oksigen sedimen, kawasan perumahan, logam berat, nutrien

Introduction

Soil and water quality are issues which affect the quality of our food, health and environment in general (Singh *et al.*, 2004). Several human activities such as discharge of untreated waste water and raw sewage, urban development, agriculture and aquaculture have directly degraded the natural environment (Sumok, 2001).

Wastewaters from residential areas are categorized into grey water and black water. The excessive of nitrogen and phosphorous may contribute to algal bloom that leads to eutrophication. The residential area and industrial discharging directly and indirectly into water resources cause excessive pollution of surface and underground water (Akcay *et al.*, 2003).

Sediment is a sink for organic materials and other contaminants such as heavy metals, antibiotics and pesticides and these contaminants could affect the quality of water which is in contact with sediment for a long time (Ling *et al.*, 2009). The excessive amount of heavy metal in sediment may lead to toxicity and it is dangerous to aquatic and human health. But certain heavy metal such as Cu and Zn are also essential biological micronutrients that are required for the growth of organisms (Ouyang *et al.*, 2002).

The residential areas including villages may give an impact on water and sediment of Semariang Batu River. This study will focuses on residential area wastewater discharge on the sediment of Semariang Batu River since there are residential area and village along the river. The main objective of this study was to investigate the impact of residential areas and cage culture on water and sediment qualities of Semariang Batu River.

The specific objectives of this study were:-

1. To determine the sediment oxygen demand values of Semariang Batu River.
2. To determine the nutrients concentrations and other sediment characteristics of sediment.
3. To determine the in-situ parameters such as pH, temperature and dissolved oxygen of the river.
4. To determine the concentrations of heavy metals of sediment at selected stations.
5. To compare results from different stations.

Literature Review

1.1 Wastewater

Wastewaters generated from residential area are divided into grey water and black water. Black water is generated from personal activities such as urine and faeces while grey water is generated from household activities such as laundering, cooking and bathing. In general, wastewater contains substantial amounts of beneficial nutrients and toxic heavy metals, which are creating opportunities and problems for agricultural production (Khan *et al.*, 2008).

According to Ling *et al.* (2009), for residential areas, discharge into the rivers includes untreated or treated sewage and grey water with high organic matter such as nitrogen and phosphorous which may results eutrophication on receiving water bodies. Anthropogenic impact on natural environments and especially on aquatic ecosystems is currently a topic of increasing concern. Deterioration of surface water and especially river water quality has recently been observed in many aquatories (Singh *et al.*, 2004). The increasing industrialization and the rapid growth of the large urban centres has been accompanied by increases in the pollution stress on the aquatic environment.

Rapid population growth, land development along the river basin, urbanization and industrialization have been subjected the rivers in Sarawak to increasing stress, giving rise to water pollution and environmental deterioration (Sumok, 2001). Degradation of river quality particularly in Sarawak includes urban development, infrastructure construction and discharge of untreated waste and raw sewage from settlement areas and aquaculture farms (Buda *et al.*, 2008).

1.2 <u>Water Quality</u>

Water quality assessment is the way to manage the surface water and assist in decision making for development or protecting the river (Sullivan *et al.*, 2002). There are many factors such as climate change, underlying geology and antropogenic activities that might influenced water quality of the river.

The discharge of organic, degradable wastewaters into flowing waters causing the decreasing of dissolved oxygen concentration. Two major causes for oxygen deficit in river water are metabolism of pollutants by microorganisms (biodegradation) and chemical oxidation of reduced pollutants (Drolc *et al.*, 1995). Organic matter may be accumulated on the river bottom and oxygen is also consumed because of respiration of plants, algae and phytoplankton. Besides that, the factors which are beneficial for dissolved oxygen concentration are atmospheric reaeration (input of oxygen from the atmosphere through river surface into water) and production of dissolved oxygen due to photosynthesis (Drolc *et al.*, 1995).

1.3 <u>Sediment in River</u>

Sediments play an important role in elemental cycling in the aquatic environment. Most sediment in surface waters derives from surface erosion and comprises a mineral component, arising from the erosion of bedrock, and an organic component arising during soil-forming processes (WHO, 1996). Generally, sediment comprises many shapes and sizes which it can be small, such as sand, small pebbles and silt, or large such as boulders, which are normally found upriver. Sediments found in estuaries are mostly fine-grained, such as sand and silt. Sediments act as both carriers and potential sources of contaminants in an aquatic environment. Industrial and household waste discharges directly or indirectly, through leakages in the sewage systems into water sources cause excessive pollution of surface and underground water (Akcay *et al.*, 2003).

1.4 Sediment oxygen demand (SOD)

Sediment oxygen demand (SOD) is the rate at which dissolved oxygen (DO) is removed from the water column in surface water bodies due to decomposition of organic matter in the bottom sediments and includes both the respiration rates of benthic communities and chemical oxidation of reduced substances in the sediments (Gin and Gopalakrishnan, 2010). SOD could be computed with the amount of oxygen consumption per unit interfacial area per unit time ($mgO_2/ m^2/ h$) (Chau, 2002).

Ling *et al.* (2009) has been reported that the mean SOD_{20} values ranged from 0.76 $gO_2 /m^2/day$ to 21.4 $gO_2 /m^2/day$ in the Semariang Batu River. According to Ling *et al.* (2009), the stations downstreams of fish aquaculture showed elevated SOD_{20} of 10.4 g $O_2/m^2/day$ when compared with the lowest value of 5.6 g $O_2/m^2/day$ upstream. A study by Gin and Gopalakrishnan (2010) reported that SOD values for a tropical reservoir in Singapore ranged from 1.4 to 3.3 g $O_2/m^2/day$.

1.5 Heavy metal

Heavy metals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Kamaruzzaman *et al.*, 2010). Heavy metals are present in streams as a result of chemical leaching of bed rocks, water drainage and runoff from the banks, and discharge of urban and industrial wastewaters (Soares *et al.*, 1999). Heavy metal contamination in sediment, soil and ground water is one the largest threat to environmental quality and human health (Li *et al.*, 2000).

The contents of heavy metals in sediments unlikely related to the corresponding contents in the aquatic phase (Cheung *et al.*, 2003). Contamination caused by heavy metal affects both ocean waters, those of the continental shelf and the coastal zone where, besides having a longer residence time, metal concentrations are higher due to the input and transport by river runoff and the proximity to industrial and urban zones (Kamaruzzaman *et al.*, 2010).

1.6 Effects of Heavy Metal

Certain heavy metals, such as Cu and Zn, are essential biological micronutrients required for the growth of organisms but other heavy metals, such as Hg, Pb and Cd, are not required for growth and have been considered to be most noxious with respect to human health and aquatic life (Ouyang *et al.*, 2002). High levels of lead, copper and iron have been found to bring rapid physiological changes in river and lake fish and continuous exposure to organisms in low concentration may result in bioaccumulation, and subsequent transfer to man by the food chain (Mendil *et al.*, 2010). Therefore, enrichment of metals in the bed sediments proved an important factor for detecting the sources of heavy metal in an aquatic ecosystem because suspended particles carried by industrial effluents and domestic sewage are ultimately deposited as the sediments containing measurable quantities of Cd, Cr, Co and Cu (Abdul Rauf *et al.*, 2009).

A study in Almendras river, Cuba by Olivares-Rieumont *et al.* (2005) reported that metal concentrations (μg/g) in sediments ranged from 86.1 to 708.8 for Zn, 39.3 to 189.0 for Pb, 71.6 to 420.8 for Cu, 84.4 to 209.7 Cr, 1.5 to 23.4 for Co, and 1.0 to 4.3 for Cd. It has been reported by Cheung *et al.* (2003) that the frequency of metals detected in the samples was Zn> Cu> Ni> Pb> Cr> Cd at different locations in Pearl River Delta, China. A study by Marcussen *et al.* (2008) on the distribution of elements of river receiving water in Hanoi, Vietnam showed that the sediment was polluted with potentially toxic elements (PTEs) with maximum concentrations of 73 As, 427 Cd, 281 Cr, 240 Cu, 218 Ni, 363 Pb, 12.5 Sb and 1240 Zn mg kg^{-1} d.w.

The average concentration of Pb and Cu at Pahang River Estuary were 74.31± 22.97 μg/g and 18.65 ±7.65 μg/g (Kamaruzzaman *et al.*, 2010). A study by Ouyang *et al.* (2001) at Cedar and Ortega river subbasin showed that concentrations of Pb ranged from 4.47 to 420.00 mg/kg dry weight, Cu from 2.30 to 107.00 mg/kg dry weight, Zn from 9.75 to 2,050.00 mg/kg dry weight and Cd from 0.07 to 3.83 mg/kg dry weight.

In the study at surface sediments (0–5 cm) from 59 stations within the Yangtze River intertidal zone by Zhang *et al.* (2009), the concentrations ranged (in mg / kg dry weight): Al, 40,803–97,213; Fe, 20,538–49,627; Cd, 0.12–0.75; Cr, 36.9–173; Cu, 6.87–49.7; Mn,413–1,112; Ni, 17.6–48.0; Pb, 18.3–44.1; and Zn, 47.6–154.

1.7 <u>Nutrients</u>

Pollution of phosphorus and nitrogen is well known to contribute to eutrophication problems of the surface water, such as rivers and lakes where human activities have long-term influence on the global pollution (Wu *et al.*, 2008). Both nitrogen and phosphorus contribute to nutrient pollution, nitrogen is the more significant driver of eutrophication in most coastal areas (Wang *et al.*, 2009).

Phosphorus discharged with effluent can enhanced the growth of organisms associated with eutrophication. Organic matter from dead plankton, organic fertilizers, uneaten feed, and excrement of culture species settles on pond bottoms and gradually mixes with soil particles (Boyd *et al.*, 2010). Sustained inputs of phosphorus or nitrogen to aquatic environments lead to increased rates of eutrophication, a widespread problem throughout the world affecting the quality of domestic, industrial, agricultural and recreational water resources (Carey and Migliaccio, 2009).

2.0 Materials and Methods

2.1 Sampling location

Samples were collected from seven stations from residential area along the Semariang Batu River. There were three sampling trips which were on 24^{th} August 2010, 6^{th} December 2010 and 19^{th} January 2011. Rainy weather was observed on 6^{th} December 2010 during the second trip. In situ parameters of the river such pH, temperature and dissolved oxygen were taken for every trip.

The sediment samples were collected at the bottom of the river during low tide. Station S1 was located at the upstream of Semariang Batu River where urban residential area was observed ; station S2 was located near Kg. Semariang Batu opposite the Jetty, near Kg. Semariang Batu ; station S3 was located downstream of a cage culture; station S4 was located at the opposite side of the Semariang River; station S5 was located upstream of Loba Kara where it was observed 4 km away from the shrimp farm ; station S6 was located at the upstream of Loba Kara River and station S7 was located at Btg. Mangkuang River.

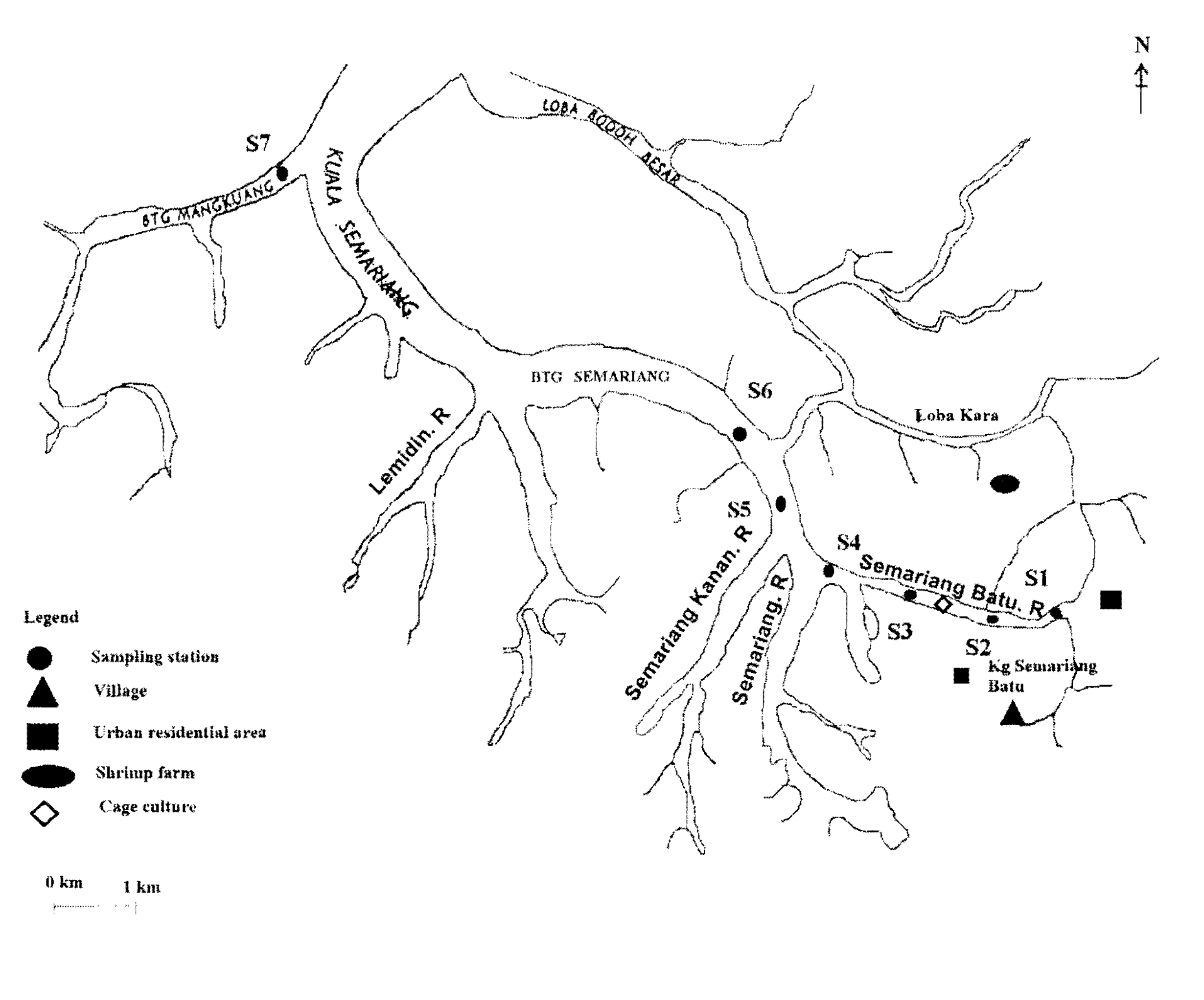

Figure 1 Map of Sampling Stations

2.2 Sediment sampling

2.2.1 SOD and sediment characteristics sampling

For SOD measurement, three undisturbed core sediment were collected and capped on the top and at the bottom with PVC caps. The inner diameter and height of sediment core were 5.1 cm and 2.7 cm. The water samples were collected by using 4 L plastic containers. Sediment samples were placed in plastic bag and preserved at 4° C prior to analysis. For sediment characteristic analysis the undisturbed sediment was collected from the bottom of the river during the low tide.

2.2.2 SOD

For SOD measurement analysis in this study, the method was followed that of Ling *et al.* (2009). As the sample was arrived at the laboratory, the sediment cores were equilibrated to room temperature. Two chambers consisting of sediment chamber and blank chamber with the height of 24.0 cm and inner diameter of 24.2 cm were set up in the laboratory. The volume of each chamber was 11 liters. The clean chambers were filled to three fourth full by using river water. Three core samples were placed in the sediment chamber and the chambers were sealed. Calibrated dissolved oxygen meter (Hanna 9142) was inserted and entrapped air was removed before sealing with silicon seal. Three chambers were set up simultaneously. The chamber was left for 10 minutes to allow suspended sediments to settle. The DO values were recorded at 10 minutes intervals for 3 hours. The SOD rate was calculated from the graph of DO concentration in the chamber versus time. The slope of the oxygen depletion line regression line was determined through linear regression. SOD was computed according to Equation [1] (Ling *et al.*, 2009).

$$SOD_T = 1.44 \frac{V}{A}(-b) \qquad [1]$$

where SOD_T = sediment oxygen demand (g $O_2/m^2/d$)

V = volume of the chamber (L)

A = surface area of sediment (m^2)

$b = b_s - b_c$,

where b_s = slope of DO concentration for sediment core

b_c = slope of DO concentration for control core

Measured SOD rates were corrected to 20°C and 25° C using van't Hoff form [Equation 2] of the Arrhenius relationship.

$$SOD_{20} = \frac{SOD_T}{1.065^{(T-20)}} \qquad [2]$$

where T= water temperature (°C)

SOD_{20} = SOD_{20} at 20° C (g O_2 / m^2/d)

SOD_T = SOD_T at temperature T (g $O_2/m^2/d$)

2.3 Parameter Analysis

The sediment samples were air-dried in the laboratory for 2 weeks and grounded with pestle and mortar. Then, the samples were sieved with 2.0 mm sieve before proceed with the analysis.

Sediment samples were analyzed for several parameters such as pH, moisture content (w), total organic carbon (TOC), total phosphorous (TP), total Kjeldahl nitrogen

(TKN) and heavy metal (Zn, Cu, Fe, Pb, Cr, Cd and Ni). In situ parameters such as pH, temperature and dissolved oxygen values was taken. All the sediment samples were analyzed in triplicate.

pH

pH of solution were carried out with 10 g of air-dry sediment with 50 mL deionized water added into the 100 ml beaker. The solution was stirred and left for 10 minutes. The electrode was inserted into the suspension on the clear supernatant above the sediment. Then, the pH reading was recorded (Sparks *et al.*, 1996).

Moisture content

By using a clean and dry weighing tin, the mass of empty tin was weighed and recorded. Then, 5 g of sediment was placed in the weighing tin and the weight was recorded. The weighing tin with sample was placed in the oven and dried to constant temperature at 105°C. The samples left for overnight. The weighing tins were removed and allowed to cool in desiccator. The weight of the dry samples was weighed. The moisture content was calculated according to equation [3],

$$W, moisture\ content = \frac{M2-M1}{M3-M1} X\ 100\ \% \qquad [3]$$

where M1 = mass of tin after 24 hours (g)

M2 = mass of sediment and tin (g)

M3 = mass of tin (g)

Organic Matter

Organic matter in the soil was determined by using Loss-on-ignition (LOI) method (Sparks *et al.*, 1996). Crucibles were heated in muffle furnace at 400° C for 2 hours. After that, 2 g of air-dried soil ground was added to the crucibles and heated for 24 hours. After 24 hours, the crucibles were put in dessicator and the weight of the crucibles was determined. Then, the samples were ignited in the muffle furnace at 400 ° C for 16 hour. The crucibles were cooled in the dessicator and the weight of the crucibles was determined. The organic matter was calculated according to equation [4]

$$\boldsymbol{OM,\% = \frac{Weight\ 105 - Weight\ 400}{Weight\ 105}\ X\ 100} \qquad [4]$$

where,

weight 105 = weight of soil sample after heating at 105 °C

weight 400 = weight of soil sample after ignition at 400° C

Total organic carbon percentage was calculated using equation [5] Boyd (1995).

$$\mathrm{TOC} = 0.58\ \mathrm{X}\ \mathrm{OM}\ (\%) \qquad [5]$$

Total Phosphorus

Total phosphorus in sediment was determined by using perchloric acid method ($HClO_4$) according to the Method of Soil analysis, Chemical Method (Sparks *et al.*, 1996) and followed by ascorbic method (Sparks *et al.*, 1996). Two grams of air-dried sample and 30 mL of 70 % $HClO_4$ were added in a beaker. The mixture was digested on a hot plate in stainless steel hood until the dark colour due to the organic matter disappeared. Then, 2 mL of $HClO_4$ was added to wash down any particle sticking to the sides of the flask. For the soil contain high organic matter content, 20 mL of concentrated HNO_3 was added and heated to oxidize the sample. When digestion completed, the beaker was removed. After that, the beaker was cooled. The mixture was diluted with deionized water to 250 mL and mixed well. The solid material was allowed to settle. The aliquot was transferred to 50 mL volumetric flask.

Ascorbic acid method

Ten milliliters of sample was transferred to 50 mL volumetric flask. Then, 25 mL of deionized water and 8 mL of mixed reagent was added. The solution was diluted to volume with deionized water the absorbance was measured at 880 nm with Hach DR4000U spectrophotometer. The total phosphorus was calculated according to equation [6]

$$TP = P \text{ concentration (mg/l)} \times \frac{50}{V1} \times 250 \text{ ml} \qquad [6]$$

where V1 = mass of sediment use (g)

TKN

Total Kjeldahl nitrogen in the sediment was determined by following the Kjeldahl (1883) method. The sediment to be analyzed for total nitrogen was dried, ground and sieved before analysis and stored in paper bags. After 0.250 g of sediment was placed in the digestion flask, 1.1 g of K_2SO_4 and 3 mL of concentrated H_2SO_4 were added and heated the flask on a hotplate. The flask with the sediment was heated for about 4 hours or until digestion became clears. After completion of digestion, the flask was allowed to cool and 20 mL of distilled water was added. The digestion was transferred to distillation unit (Buchi Autokjeldahl Unit K-370a) and distilled about 3 minutes. The distillate was collected and 20 mL of boric acid was added. Then, 100 mL of distillate was added with 2 drops of mixed indicator and the NH^{+}_4 were determined by titration with 0.02 M HCl. The color change at the end point was observed from green to pink. Total Kjeldahl Nitrogen was calculated according to equation [7]

$$\% \text{ TKN} = \frac{\text{mol HCL X molarity HCL X 100}}{\text{0.02M X weight of sediment}} \qquad [7]$$

Heavy Metals

Sample digestion

For heavy metal analysis in sediments, the method was followed that of Hseu *et al.* (2002). Sediment samples were air dried for 2 weeks in the laboratory. The sample was ground by using mortar and pestle. Then, 1 g of sample was weighed and placed into a 50 ml beaker. After that, 5 mL of concentrated nitric acid and 15 mL hydrochloric acid were added. A few drops of 35 % of H_2O_2 were added to destroy organic matter. The samples were digested on the hot plate for 3 hours.

After digestion, the sample was removed to cool before it was diluted with deionized water into a 100 mL volumetric flask. The solution was transferred into polyethylene bottle and kept in refrigerator at 4°C. The extracted solution was analyzed for Zn, Cu, Cr, Fe, and Pb. The concentration of Zn, Cu, Cr, Cd, Fe, Ni and Pb was determined by using atomic absorption spectrometer ThermoScientific (AAS). The standard concentration of heavy metals standard with their detection limits are shown below:-

Table 1: Heavy metal standard concentration and their detection limits

Heavy Metal	**Standard 1(mg/L)**	**Standard 2 (mg/L)**	**Standard 3 (mg/L)**	**Detection Limits (mg/L)**
Zn	1	3	6	0.0033
Cu	1	3	6	0.0045
Cr	1	3	6	0.0054
Pb	1	3	6	0.0130
Fe	1	3	6	0.0043
Ni	1	3	6	0.0080
Cd	1	3	6	0.0028